Mean-field lattice equations of state: 5. Influence of pressure on liquid–liquid phase behaviour of polymer blends

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(Received 29 March 1990; revised 5 August 1991; accepted 1 October 1991)

The semi-phenomenological (SP) treatment and a modified form of the mean-field lattice-gas (MFLG) model were used to investigate the influence of pressure on the phase behaviour of polymer blends. It was shown that the peculiar phase relations of the system poly(ethyl acrylate)/poly(vinylidene fluoride) could be reproduced in a qualitative way. Positive and negative signs for the excess volume could be predicted in accordance with the observed pressure–temperature–weight fraction relations. Furthermore the effect of pressure on the location of binodals for oligomeric mixtures of polybutadiene and polystyrene was represented quantitatively with the MFLG model and the SP treatment. It was shown that end group contributions cannot be neglected if polymers of low molar mass are involved. It was further demonstrated that the SP approach only requires one interaction function to represent all critical data whereas in the MFLG model different interaction terms, one for each system, are necessary in order to obtain good descriptions. Both descriptions are found to be superior to a modified version of the Flory equation of state theory.

(Keywords: equation of state; behaviour; blends)

INTRODUCTION

Equilibrium thermodynamics offers a powerful tool in the understanding of phenomena occurring during polymer processing and manufacture. Pressures building up during polymer blending may turn a two-phase blend into a homogeneous one-phase melt and vice versa. *Figure 1a* illustrates such implications for the system poly(ethyl acrylate)/poly(vinylidene fluoride) (PEA/PVDF). The figure is based on experimental data reported by Suzuki *et al.*[1]. Situation A represents a two-phase system at ambient pressure where the pressure built up during extrusion may homogenize the blend. As a result an intended two-phase extrusion cannot be realized. At a different blend composition (B) the reverse effect may occur.

From a technological point of view models which yield information on how thermodynamic properties are affected by pressure, e.g. the sign and magnitude of the excess volume during blending, are important. In previous publications[2,3] an old approach was reinvestigated[4]. It is the so-called semi-phenomenological (SP) treatment since it defines the pressure dependence of the interaction function in the rigid lattice model with classical thermodynamic relationships of general validity. One could look upon this treatment as a sort of 'breathing' rigid lattice: the number of lattice sites remains constant but their volume changes with pressure. As a consequence the excess volume can be non-zero, which is an impossible feature for the rigid lattice model. Other models like the mean-field lattice-gas model (MFLG)[5–7] introduce holes (or empty sites) into the lattice. As a result an equation of state (EOS) can be derived.

The performance of the SP treatment has recently been compared to the MFLG model with the aid of the phase behaviour and its relation to the pressure for the system polystyrene/cyclohexane[2]. In the sign of $(\partial T/\partial p)$ at the critical point changes on an increase in pressure and in molar mass. The SP treatment did quite well. If the parameters were adjusted to data on the pressure–$(\partial T/\partial p)$ relation for one molar mass it correctly predicted the influence of the molar mass on $(\partial T/\partial p)$. The MFLG model performed less well. Only if the interaction term was allowed to depend strongly on the hole concentration could the MFLG model reproduce the phase diagram, and then only qualitatively. In this paper we investigate whether pressure–temperature–weight fraction (p–T–w) relations in polymer blends can be represented by the SP and the MFLG treatments. Literature data on two systems were studied: PEA/PVDF[1] and oligomeric mixtures of polystyrene (PS) and polybutadiene (PB)[8].

Schneider schematically classified liquid–liquid equilibria with respect to pressure, temperature and concentration into 14 categories (see ref. 9, Figure 5). The phase behaviour of the system PEA/PVDF belongs to none of these categories. *Figure 1b* summarizes the data in terms of p–T curves at constant composition (isopleths). Miscibility may improve or decline with increasing

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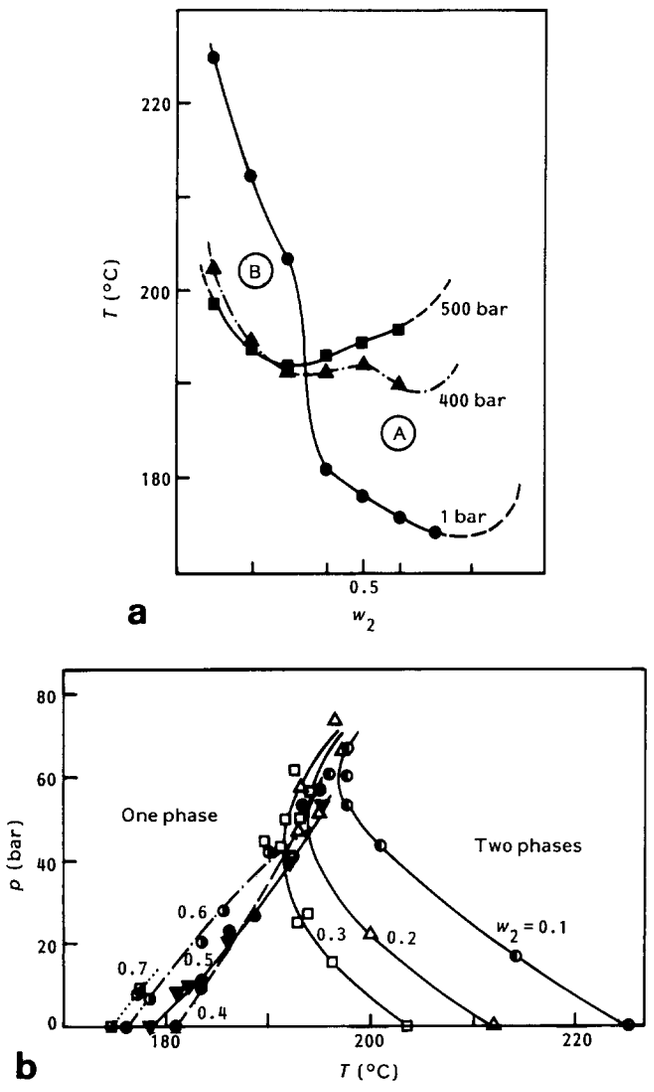

Figure 1 Experimental p–T–w relations for the system PEA/PVDF: (a) isobaric T–w sections; (b) isopleths for the indicated mass fractions of PVDF

pressure depending on the blend composition. An important consequence of this peculiar phase behaviour is that contraction [negative curvature in $\Delta V^E(w_2)$] and expansion (positive curvature) upon mixing must both occur. Such behaviour is a severe test for any molecular model. Except for reference 1 few experimental results on the system PEA/PVDF exist in the literature. Endres *et al.* and Li *et al.* used X-ray scattering, optical microscopy and calorimetric techniques to determine the phase diagram for the system in hand[10,11]. They reported a binodal and a spinodal of the lower critical solution temperature (*LCST*) type and their interference with the crystallization of PVDF at 1 bar*. Furthermore it was found that the mixture is characterized by a positive excess volume of mixing at 1 bar, $T = 183$°C and for PVDF concentrations of 30, 40 and 50 wt%. These data seem to be in agreement with the observations of Suzuki *et al.*[1] since they refer to situation B in *Figure 1a*. Paul *et al.*[12] investigated blends containing PVDF. It was found that all the systems studied (e.g. with PEA) show *LCST* behaviour. A cloud-point curve (CPC) was reported at 1 bar in the same temperature region as found by Endres *et al.*[10]. Finally Briber and Khoury[13] reported a phase diagram for PEA/PVDF in which the interference of the lower-critical liquid–liquid range with the solubility curve for PVDF is clearly shown. No further attention will be paid to their cloud-points since the curves refer to one branch of the CPC only. In fact only the data by Suzuki *et al.*[1] and Li *et al.*[11] will be considered since they contain information on the pressure influence on the phase behaviour of PEA/PVDF.

Rostami and Walsh[8] reported data on the effect of pressure on the miscibility of oligomeric mixtures of PB and PS. These systems show upper critical solution temperature (*UCST*) miscibility behaviour and the application of pressure causes the temperature range of partial miscibility to increase. The authors described a procedure for the calculation of binodals and spinodals at different pressures with a modified form of the EOS theory of Flory. The sign of the effect of pressure was correctly predicted but the description of the experimental data, however, was rather poor.

In the following the SP treatment and a modified form of the MFLG model were applied to describe the pressure effect on the phase behaviour of PEA/PVDF and PB/PS.

Only a brief introduction on the SP and the MFLG treatments will be given here since they have both been thoroughly discussed in previous papers[2,5–7].

The calculations were performed with a parameter estimation computer program developed at DSM Research.

THE SP MODEL

In the SP approach[2] the general relationships for the thermal expansion coefficient α, the isothermal compressibility β and the excess volume ΔV^E:

$$\alpha = (1/V)(\partial V/\partial T)_p \quad (1)$$

$$\beta = -(1/V)(\partial V/\partial p)_T \quad (2)$$

$$\Delta V^E = (\partial \Delta G/\partial p)_{T,n_i} \quad (3)$$

serve to define $g(p, T, \phi_2)$ in the Flory–Huggins–Staverman expressions for the Gibbs free enthalpy, ΔG, of mixing two polydisperse polymers 1 and 2:

$$\Delta G/(N_\phi RT) = \sum_i (\phi_{1i}/m_{1i}) \ln \phi_{1i} + \sum_i (\phi_{2i}/m_{2i}) \ln \phi_{2i} + g\phi_1\phi_2 \quad (4)$$

where g represents the interaction function.

Assuming that α and β are constant and representative for the pure components as well as for the mixture, we can deduce[2] a general form for g:

$$g = \left(\frac{A + BT + CT^2}{T}\right)(D + Ep + Fp^2) \quad (5)$$

where A, B, C, D, E and F are coefficients to be determined from experimental data. Equation (5) demonstrates that any parameter in a theoretical expression for g may be expected to depend on p and/or T.

THE MFLG MODEL

The MFLG treatment retains the basic volume unit of the rigid lattice and introduces empty sites at random to account for variations in volume without a change in the

* 1 bar = 1×10^5 Pa

amount of matter[7]. The Helmholtz free energy ΔA of mixing n_0 vacant sites and n_1 and n_2 sites occupied by molecules 1 and 2, reads

$$\Delta A/(N_\phi RT) = \phi_0 \ln \phi_0 + (\phi_1/m_1) \ln \phi_1 + (\phi_2/m_2) \ln \phi_2 + g_1\phi_0\phi_1 + g_2\phi_0\phi_2 + g_{12}\phi_1\phi_2 \quad (6)$$

where

$$g_i = a_i + b_i/Q$$
$$g_{12} = a_{12} + b_{12}/Q$$
$$b_i = b_{i,0} + b_{i,1}/T$$
$$b_{12} = (b_{12,0} + b_{12,1}/T)(1 - c_1)(1 - c_2)$$
$$Q = 1 - c_1\phi_1 - c_2\phi_2$$

and

$$c_i = 1 - \frac{s_i}{s_0}$$

The concentration variables for holes, and molecules 1 and 2 are indicated by ϕ_0, ϕ_1 and ϕ_2, respectively. The introduction of different molecular surface areas (s_0 for holes and s_1 for segments i) and the assignment of different numbers of segments (m_i) make an abstraction of the lattice. Furthermore the interaction terms between like and unlike segments are represented by $b_{i,1}$ and $b_{12,1}$, respectively; a_i, $b_{i,0}$, a_{12} and $b_{12,0}$ are empirical parameters which, however, can be shown to have a physical significance[2,6]. In order to reproduce the pressure effect on the phase behaviour of the systems in hand, it was found necessary to define a dependence of a_{12} on the hole concentration:

$$a_{12} = a_{12,0} + a_{12,1}\phi_0 + a_{12,2}\phi_0^2 \quad (7)$$

The usual procedures lead to spinodal and critical conditions and the conditions for equilibria between two phases. They can be found in reference 2. The EOS is given by

$$-\frac{pv_0}{RT} = \ln \phi_0 + [1 - (1/m_1)]\phi_1 + [1 + (1/m_2)]\phi_2 + (a_1\phi_1 + a_2\phi_2)(\phi_1 + \phi_2) + (b_1\phi_1 + b_2\phi_2)(Q - \phi_0)Q^{-2} - (a_{12} + b_{12}TQ^{-2})\phi_1\phi_2 \quad (8)$$

POLY(ETHYL ACRYLATE)/POLY(VINYLIDENE FLUORIDE)

SP treatment

If we assume that the polymers involved are monodisperse and the interaction function is linearly dependent on the concentration of one of the components

$$g = g_0 + g_1\phi_2 \quad (9)$$

we can derive spinodal and critical conditions for a strictly binary system[14]

$$\text{spinodal} \quad \frac{1}{m_1\phi_1} + \frac{1}{m_2\phi_2} = 2[g_0 - g_1(1 - 3\phi_2)]$$
$$\text{critical state} \quad \frac{1}{m_1\phi_1^2} - \frac{1}{m_2\phi_2^2} = 6g_1 \quad (10)$$

The experimental data in *Figure 1* are significant enough to roughly estimate the critical locus (*Figure 2*). If the temperature dependence of g is limited to g_0 we conclude that the critical curve requires g_1 to be at least a quadratic function of p. Further, the minimum w_2^* value at p^* supplies a relation between the coefficients and allows g_1 to be written as

$$g_1 = g_{10} + g_{11}p[1 - (p/p^*)] \quad (11)$$

Employing the usual first approximation for the temperature dependence of g_0, we note that g_0 must depend on pressure because of the changes in shape the miscibility gap undergoes when the pressure is varied. Writing a quadratic dependence we have

$$g_0 = g_s + g_h/T \quad (12)$$

with

$$g_h = g_{h,0} + g_{h,1}p + g_{h,2}p^2$$

Equations (9)–(12) contain six adjustable parameters. Two critical points (indicated by arrows in *Figure 2*) were selected to determine four of them. To find values for the two remaining coefficients, two cloud-points were employed. Per cloud-point there are two equations and an additional unknown, namely the concentration of the coexisting phase. Parameter values are given in *Table 1*.

Complete isopleths (constant composition) could then be calculated and it is seen in *Figure 3* that the peculiar phase behaviour of the system PEA/PVDF is reproduced in a qualitatively correct manner.

The excess volume, defined by equation (3), is given by

$$\Delta V^E = g_{h,1} + 2g_{h,2}p + g_{11}T[1 - 2(p/p^*)] \quad (13)$$

It can be shown that the value of $N_\phi R$ in this case is close

Table 1 PEA/PVDF. Parameter values in the SP model calculated with two critical and two cloud-points

$g_{1,0}$	3.0289×10^{-3}
g_{11} (bar^{-1})	-1.4181×10^{-5}
g_s	3.1703×10^{-2}
$g_{h,0}$ (K)	-1.4687×10^{1}
$g_{h,1}$ (K bar^{-1})	5.7840×10^{-3}
$g_{h,2}$ (K bar^{-2})	-6.8047×10^{-6}

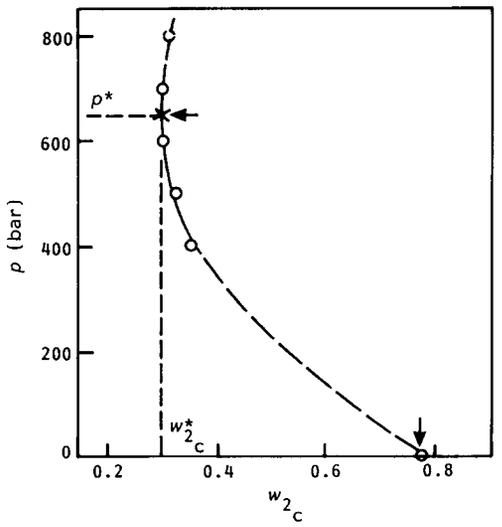

Figure 2 Estimated critical locus in the system PEA/PVDF based on the isopleths in *Figure 1b*. The two critical states used in the calculation of the SP and MFLG parameters are indicated by arrows

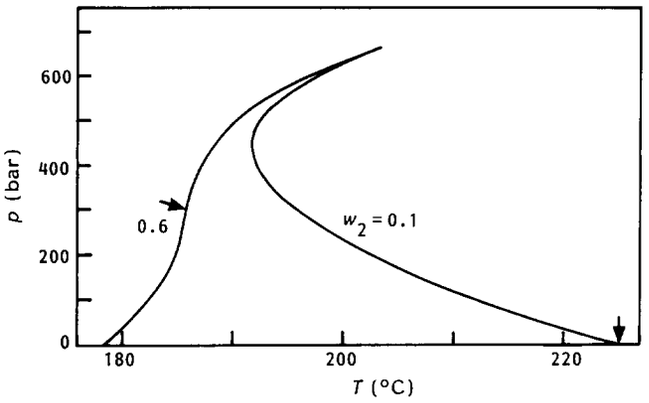

Figure 3 Isopleths for the system PEA/PVDF calculated with the SP model (see text). Arrows indicate cloud-points used to calculate parameter values

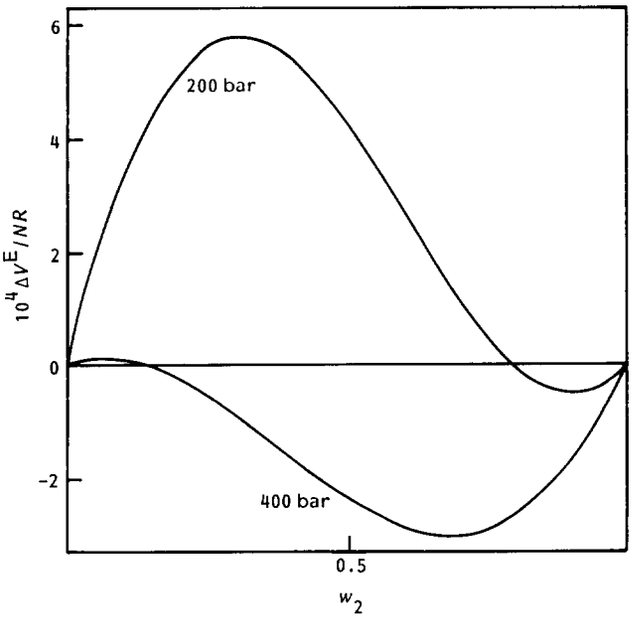

Figure 4 Excess volume predicted for PEA/PVDF with the SP model at 190°C for the indicated pressures (parameter values in *Table 1*)

to unity and, thus, can be ignored. *Figure 4* shows that the calculation is consistent since contraction upon mixing ($\Delta V^E < 0$) results in miscibility improving with increasing pressure.

MFLG model

Equation (6) contains pure component parameters besides some parameters for the mixture. The former have to be adjusted to p–V–T data. But, since no experimental information on the specific volume for PEA and PVDF exists some assumptions had to be made regarding these parameters. First of all the empirical parameters $b_{i,0}$ and a_i were set equal to zero and $b_{i,1} = 1100$. Further, the number of segments were assigned arbitrary numbers, namely $m_1 = 500$ and $m_2 = 600$. Finally, preliminary results indicated that the disparity in size of the two repeat units in the system could not be ignored: $c_1 = -1.65$ and $c_2 = -1.2$.

The same procedure as for the SP model was carried out here. Two critical points allowed the determination of four parameters of the mixture (per critical point there are three equations and one additional unknown, namely the hole concentration). One cloud point suffices to find a value for the remaining parameter. Adhering to the SP procedure, i.e. using two cloud-points, we introduce an additional parameter, $b_{12,2}$,

$$g_{12} = a_{12} + (b_{12,0} + b_{12,1}/T + b_{12,2}T)Q^{-1} \quad (14)$$

The parameter values are listed in *Table 2*.

Some isopleths for mass fractions of PVDF ($w_2 = 0.1$, 0.6 and 0.9) are shown in *Figure 5*. The p–T–w relations are reproduced in a qualitative way although the behaviour of low and high compositions is less obvious compared to the experimental data or the SP treatment (*Figure 3*). *Figure 6*, in addition, shows some binodals calculated at 1 and 300 bar the location of which does not conform to the experimental situation. The observed bimodal curves in *Figure 1a* are not reproduced either. This is not unexpected[15] since two-peaked curves can be calculated only if the interaction function depends more strongly on concentration than merely on the factor Q.

The excess volume in the MFLG model is defined as

$$\Delta V^E = V_m - x_1 V_1 - x_2 V_2 \quad (15a)$$

where V_m, V_1 and V_2 are the volumes of the mixture and the pure components 1 and 2, respectively. Using equations (8) and (15a) and

$$V_m = \frac{m_2 w_2 v_0}{\phi_2} \quad (15b)$$

then ΔV^E can be calculated. It is seen in *Figure 7* that negative as well as positive values are obtained. The MFLG values for ΔV^E however, are 10 times as large as the values calculated with the SP model. Only Endres *et al.*[10] reported some experimental data on ΔV^E for

Table 2 PEA/PVDF. Parameter values in the MFLG model calculated with two critical and two cloud-points

$a_{12,0}$	-4.3786×10^{-2}
$a_{12,1}$	7.3757×10^{-1}
$a_{12,2}$	-2.4963
$b_{12,0}$	-9.0417×10^{-2}
$b_{12,1}$ (K)	-6.9603×10^{-1}
$b_{12,2}$ (K^{-1})	1.9625×10^{-4}

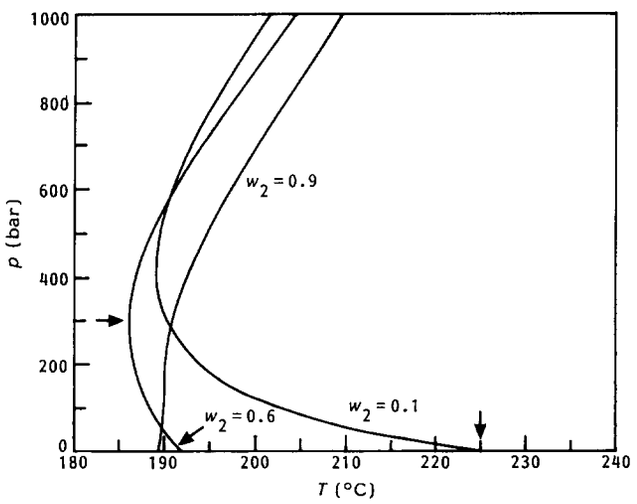

Figure 5 Isopleths for the system PEA/PVDF calculated with the MFLG model (see text). Arrows indicate cloud-points used to calculate parameter values

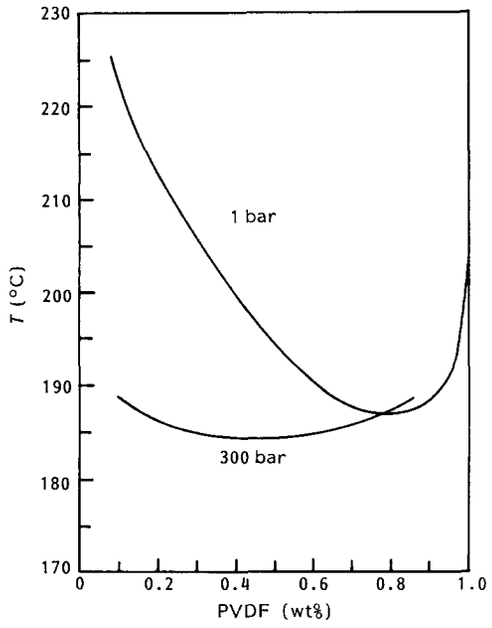

Figure 6 Calculated binodals in the MFLG model for the system PEA/PVDF (parameter values in *Table 2*)

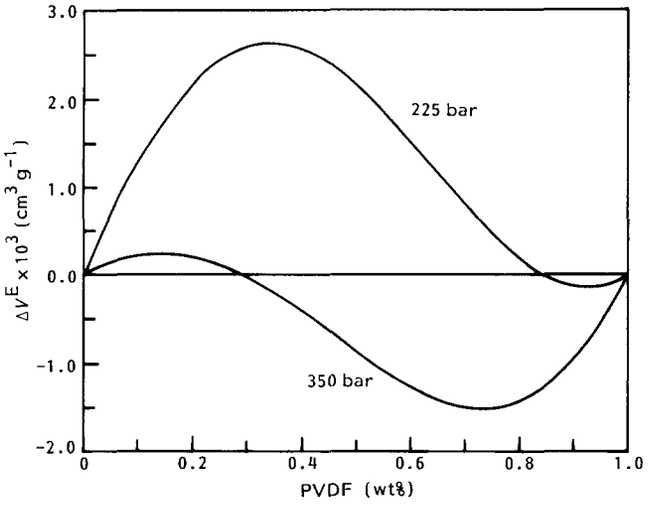

Figure 7 MFLG excess volumes at 190°C for the indicated pressures (parameter values in *Table 2*)

PEA/PVDF at 183°C and 1 bar. The MFLG values are about twice as large as the experimental values, namely 0.0115 cm^3 g^{-1} (MFLG) and 0.0047 cm^3 g^{-1} (expt) for a 1:1 blend. With the values for the parameters in the SP model (*Table 1*) the ΔV^E at 183°C and 1 bar is 0.00065 cm^3 g^{-1}, i.e. about eight times smaller than the experimental value.

OLIGOMERIC MIXTURES OF PB AND PS

MFLG treatment

Rostami and Walsh[8] reported binodal points at 1 and 1000 bar for five PB/PS mixtures of low molar mass (*Table 3*). Here it is investigated whether a modified form of the MFLG model can reproduce the effect of pressure on the phase behaviour of PB/PS.

Equation (6) contains five parameters for the pure polymers. Since for PS an extensive amount of experimental data for different molecular mass distributions exists all five parameters could be calculated[16]. However, other polymers have not been so thoroughly examined and an additional equation is required to obtain an unambiguous fit.

Beckman investigated the so-called Bondi constraint[17],

$$\frac{M_i(1-c_i)d_i}{M_S(1-c_{PS})d_{PS}} = \frac{s_{B,i}}{s_{B,S}} \tag{16}$$

where $d_i = m_i/M_i$ and M_i denotes the molar mass of the chemical repeat unit i. The subscripts i and PS refer to the substance being examined and to the material parameters for PS, respectively, with S standing for the repeat units in PS. The molecular surface areas are calculated using Bondi's group estimation method[18]. The experimental data for PB[19] were fitted using equation (16) and the EOS. The values of the parameters for PS and PB are listed in *Table 4*.

It is known from previous work[2,20] that the MFLG model is not suited to cope with the influence of pressure and molar mass on the location of the miscibility gaps of polymer solutions simultaneously unless the interaction term is a complicated function of the hole concentration. Since the latter leads to a very complicated EOS an alternative procedure was applied.

First the parameters for four mixtures of PB/PS (1 and 3–5 in *Table 3*) were determined following a similar route as for PEA/PVDF, namely adjustment of the parameters to two critical and two cloud-points at 1 and 1000 bar. The top of the curve drawn through the experimental cloud-points was assumed to be close enough to the critical point to allow identification.

The parameters for the mixtures are collected in *Table 5*. *Figure 8* compares theory and observation: a fair description was obtained. A comparison between the MFLG model and Flory's theory as applied by Rostami and Walsh (ref. 8, Figures 1–5) shows that the former is clearly superior. Binodal and spinodal curves calculated with the Flory theory are too sharp and their location is not correct.

Inspection of the parameters for the four mixtures in *Table 5* indicate that they are different for the four systems. This effect might reflect an influence of molar mass of the constituents and can be understood if one

Table 3 Characteristics of the PB/PS blends

No	Mixture[a]
1	PB920–PS1200
2	PB920–PS1520
3	PB920–PS3900
4	PB2350–PS1200
5	PB2350–PS1520

[a]Numbers indicate molar masses of the polymers

Table 4 Values for the MFLG parameters for pure PS and PB

	PS	PB
m_i[a]	3.701	2.155
c_i	−1.0889	−1.4099
a_i	−6.8354	−14.150
$b_{i,0}$	10.157	24.726
$b_{i,1}$ (K)	2318.7	2848.4

[a]Per monomer unit

Table 5 Values for the MFLG parameters for PB/PS mixtures

No.	$a_{12,0}$	$a_{12,1}$	$a_{12,2}$	$b_{12,0}$	$b_{12,1}$ (K)	$b_{12,2}$ (K^{-1})
1	0.22508	−1.3391	3.5420	0.31604	−51.310	−0.76925
3	0.02433	−0.8803	0.7984	0.20227	−33.251	−0.33885
4	0.06617	−1.0537	1.7679	−0.0446	9.6335	−0.03092
5	0.08769	−1.0583	1.6826	0.2664	−45.753	−0.49478
2	0.1640	−1.1989	2.7077	0.2814	−45.815	−0.6384

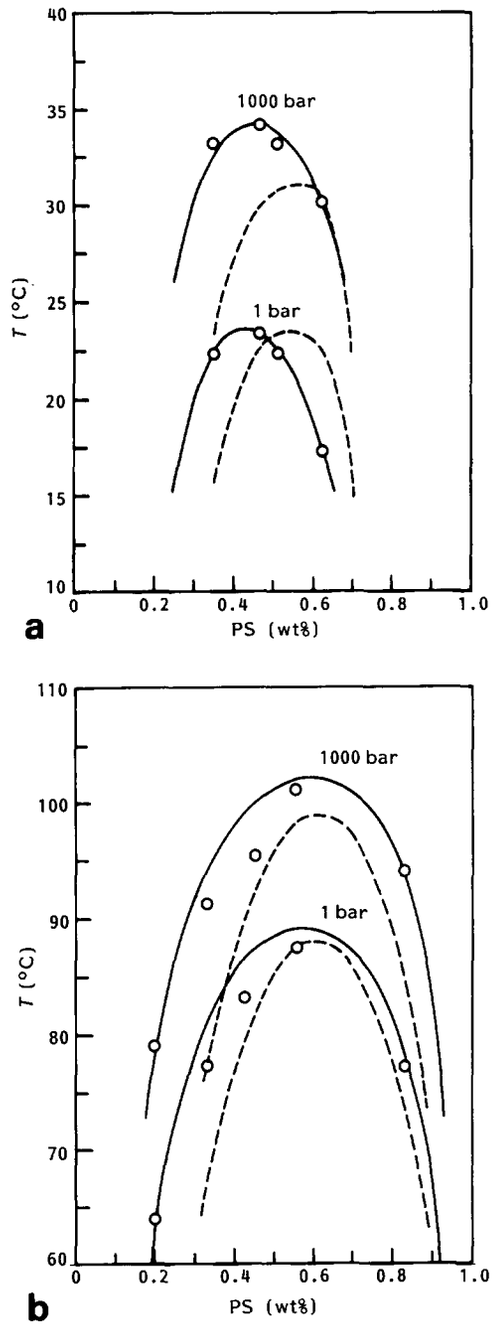

Figure 8 Oligomeric mixtures of PS and PB. Binodals at 1 and 1000 bar calculated with the MFLG model (——) and the Flory theory (---)[8]: (a) PB920/PS1200; (b) PB2350/PS1520. (○) Experimental binodal points from reference 8

realizes that with relatively short chains the influence of end groups cannot always be neglected. This was recently illustrated by an analysis of solutions of PS ($M = 4\ kg\ mol^{-1}$) in n-alkanes and alcohols[21]. For oligomeric polymers these end group effects will certainly be present. A polymer of low molar mass could be thought of as a copolymer. For instance, anionic PS is usually synthesized with butyllithium as the initiator. As a result one of the end groups is a butyl group. For a molar mass of 1.2 kg mol^{-1} this means that for every 11 styrene repeat units there is one alkyl end group. This will not only influence the sum of interactions but also the entropy term.

In the rigid lattice the chain-length dependence of the interaction term can be derived as[21]

$$g = \frac{z_1 z_2 \Delta w_{12}}{RT} \tag{17}$$

where Δw_{12} is the interchange energy between segments 1 and 2 and z_i represents the number of contacts of species i

$$z_i = z - 2 + 2/m_i \tag{18}$$

where z is the coordination number of the lattice and m_i is the number of segments of species i. In the derivation of equations (17) and (18) the difference in molecular surface area between species 1 and 2 was ignored. Using equations (17) and (18) we can express $b_{12,i}$ in equation (6) in a first approximation by

$$b_{12,i} = A + B/m_1 + C/m_2 \tag{19}$$

The constants A, B and C are obtained from the four sets of parameters in *Table 5* and permit the calculation of $b_{12,i}$ for mixture 2. The entropy parameters were assumed to depend inversely on m_2 for mixtures 1 and 3:

$$a_{12,i} = D + E/m_2 \tag{20}$$

This MFLG model including end group contributions contains 25 adjustable parameters. After the contributions in equations (19) and (20) are calculated, the parameters for mixture 2 can be predicted (*Table 5*). Calculated binodals at 1 and 1000 bar are shown in *Figure 9* and are compared to experimental data[8]. The location of the curves is ~ 7°C too high. However, when e.g. the value of $b_{12,0}$ is lowered by 0.001 to 0.28040 the prediction becomes easily quantitative.

The main reason for this defect is that the parameters of the mixture could be subject to errors up to 5% since the data involved are rather scarce. Furthermore one should bear in mind that the parameters for pure PB are adjusted to p–V–T data for a sample of M = 100.0 kg mol^{-1}. The values of these parameters may not be correct for the low molar masses of PB involved.

SP treatment

In the previous section it was shown, confirming the findings in the previous paper in this series[2], that the MFLG model cannot represent the dependence of the phase behaviour of polymer systems on pressure *and* molar mass of the polymer with a single set of parameters. Though the calculations with the MFLG model on the

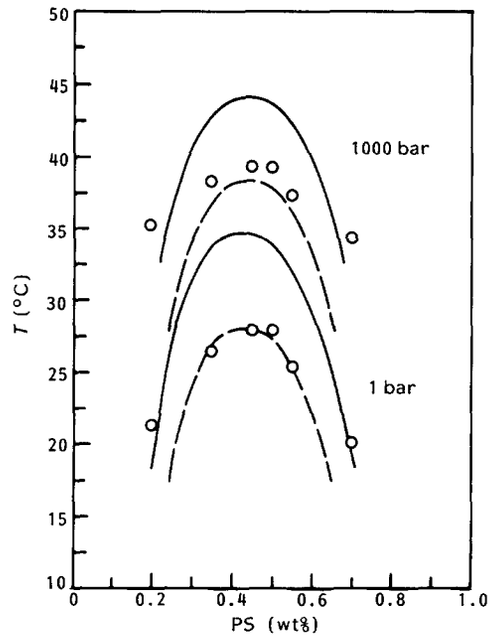

Figure 9 Prediction of binodals with the MFLG model at 1 and 1000 bar for mixture 2 in *Table 3* (parameter values in *Table 5*): (○) experimental binodal points from reference 8; (——) predicted binodals with $g = 0.28143$; (– – –) predicted binodals with $g = 0.28040$

system PB(1)/PS(2) indicated the importance of end groups, we tried here in the first instance the simpler route, simulating the pressure dependence by the usual interaction function in the SP treatment[2]:

$$g = a + \frac{b}{1 - c\phi_2} \qquad b = b_0 + b_1/T \tag{21}$$

where a and b are empirical entropy corrections, $c = 1 - s_2/s_1$ with s_i the surface area of segments i and b_1 is a measure of the interaction for 1–2 contacts. The parameters b_0 and b_1 were made linear in pressure

$$b_i = b_{i0} + b_{i1}p \qquad i = 1, 2 \tag{22}$$

When the oligomers are assumed to be monodisperse, the spinodal and critical conditions read:

$$\text{spinodal} \qquad \frac{1}{m_1\phi_1} + \frac{1}{m_2\phi_2} = 2\left[a + \frac{b(1-c)}{(1-c\phi_2)^3}\right] \tag{23}$$

$$\text{critical point} \qquad \frac{1}{m_1\phi_1^2} - \frac{1}{m_2\phi_2^2} = 6\frac{b(1-c)c}{(1-c\phi_2)^4} \tag{24}$$

where m_1 and m_2 are the number of segments in PB and PS molecules, respectively. Weight fractions are the concentration variables while m_i is calculated on the basis of the molar mass of butadiene, $m_i = M_i/55$ (M is molar mass of the polymer). The parameters in equations (21)–(24) were adjusted simultaneously to the critical data at 1 and 1000 bar for the systems in *Table 3*. A poor description, however, was obtained even when a was allowed to depend on concentration.

Next, in order to take into account end group effects in the oligomeric mixtures, b_1 in equation (21) was arbitrarily chosen to depend on m_1 and m_2. Thus, using the formalism of equations (17) and (18), we wrote for b_1

$$b_1 = A + B/m_1 + C/m_2 \tag{25}$$

In addition, we allowed b_0 in equation (22) and A to depend on pressure in a linear fashion

$$A = A_0 + A_1 p \tag{26}$$

and, thus, construct a SP treatment with eight parameters. Like before, all critical data at 1 and 1000 bar for the systems in *Table 3* were fitted with equations (21)–(26).

The procedure led to a description of the data which can be considered satisfactory when it is recognized that the measurements are represented by a single interaction term. The MFLG model, on the other hand, required one g-function per system (previous section).

Parameter values are listed in *Table 6*. Note the value calculated for s_2/s_1 (1.022) which differs substantially from that in the group estimation method by Bondi[18] (0.791).

Figure 10 displays binodals at 1 and 1000 bar predicted with the parameter values in *Table 6* for the system PB920/PS1200. The miscibility gaps are too sharp compared to the experimental data[8]. Further, the SP treatment seems to perform less well than the MFLG model (*Figure 8a*). This is not unexpected since the parameter values in the MFLG treatment were obtained from critical data as well as cloud points. If quantitative descriptions of binodals are to be obtained with the SP approach, it is likely that an additional concentration dependence of g should be introduced [see e.g. equation (9)]. It was not considered worthwhile to pursue the matter in further detail because of the lack of experimental data.

Table 6 Parameter values in the SP approach for the system PB/PS (see text)

s_2/s_1	1.022876
a	-0.49418×10^{-2}
b_{00}	0.51473×10^{-1}
b_{01} (bar^{-1})	-0.38950×10^{-5}
A_0	−13.142
A_1 (bar^{-1})	0.17501×10^{-2}
B	270.45
C	321.25

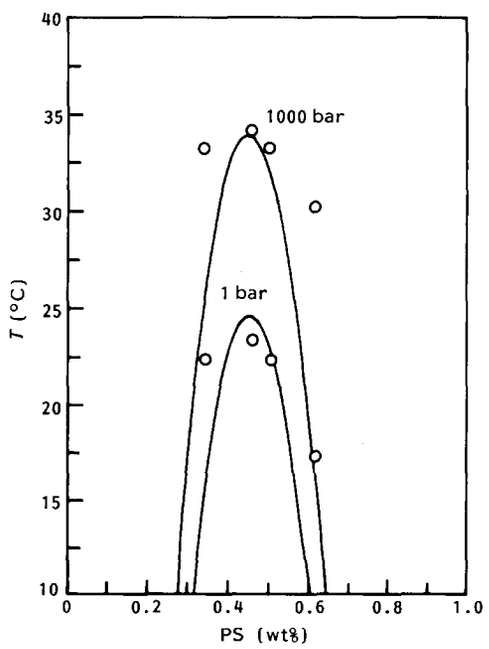

Figure 10 Predicted binodals (——) at 1 and 1000 bar in the SP treatment for the system PB920/PS1200 compared to experimental data (○)[8] (parameter values in *Table 6*)

We consider, however, that it has again been demonstrated[2] that the SP treatment is superior to the MFLG model in representing phase behaviour and its relation to pressure as well as molar mass and we prefer the SP description.

CONCLUSIONS

It was investigated whether the SP and MFLG treatments could represent the pressure effect on the $p-T-w$ relations for the system PEA/PVDF and oligomeric mixtures of PB/PS.

The SP and modified MFLG approaches both reproduce the pressure effect on the phase behaviour of PEA/PVDF in a qualitative way. The SP treatment performed slightly better than the MFLG model. In both treatments negative as well as positive values for ΔV^E are predicted, which is in qualitative agreement with the experimental data on the pressure dependence on the location of the miscibility gap[1]. It should be emphasized that both models were applied under severe simplifying assumptions. For oligomeric mixtures of PB/PS it was tested with the MFLG model whether end groups contribute to the Helmholtz free enthalpy of mixing. Adjustment of the MFLG parameters for four mixtures to critical and cloud-points served to determine those for a fifth mixture using a rough model to estimate end group contributions. Predicted binodals at 1 and 1000 bar for this mixture showed a semi-quantitative agreement. It may also be concluded that, in this case, the MFLG model performed better than Flory's EOS theory.

Further, evaluation of the critical data on these systems with the SP approach demonstrated the importance of end group contributions and, thereby, confirms the MFLG results. Finally, it should be concluded that the SP treatment is a most promising route to represent the dependence of phase behaviour on pressure as well as molar mass, and should perhaps be preferred to the MFLG model.

ACKNOWLEDGEMENT

The authors thank Dr L. A. Kleintjens (DSM, Geleen) for helpful discussions. L. van Opstal thanks DSM for a PhD grant (Universitaire Intelling Antwerpen).

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